Carbon Nanohoops

Shortest Segment of a Carbon Nanotube Synthesized

The shortest carbon nanotube, a one molecule high carbon "nanohoop," has been synthesized in the Biomolecular Materials Program by the research group of Carolyn Bertozzi in a Molecular Foundry User project. The tiny ring of carbon, called cycloparaphenylene (see figure), could have an impact on the development of faster electronic devices, more powerful sensors, and other advanced technologies.

Carbon nanotubes are hollow wires of pure carbon about 50,000 times narrower than a human hair. They can be semiconducting or metallic depending on their structure. Their unique properties could possibly be used to make faster and smaller computers, or tiny sensors powerful enough to detect a single molecule. However, carbon nanotubes have not yet made inroads into the electronics or other sectors, in part, because they are difficult to make with defined structures in large quantities. At present, they are produced in batches, with only a handful of nanotubes in each batch possessing the desired characteristics. This approach works well for laboratory research, but is too inefficient for commercial applications.

Cycloparaphenylene synthesis offers a more targeted approach. This family of benzene-derived compounds forms the smallest possible carbon hoop structure, one molecule high. It also has a fixed diameter and orientation, the two variables that determine a nanotube's electronic properties. Because of this, cycloparaphenylene molecules could possibly be used as seeds or templates to grow large batches of carbon nanotubes with precisely defined structures. Unfortunately however, this hoop-shaped chain of benzene molecules had eluded synthesis, despite numerous efforts, since it was theorized more than 70 years ago.

The heart of the synthetic challenge lies in overcoming the strain energy required to bend a string of benzene rings — which normally resist bending — into a hoop. The strain is considerable and increases with decreasing ring size: 5, 28, and 47 kcal/mol for hoops with 18, 12, and 9 benzene units, respectively. The team used a strategy that involved the build- up of strain sequentially during the synthesis, using carefully selected small molecule precursors in combination with a cyclohexadiene molecule designed to provide the curvature and rigidity necessary for the ring to form. The strategy was successful and rings with 5, 8, and 14 benzenes were obtained in good yield (>35%).

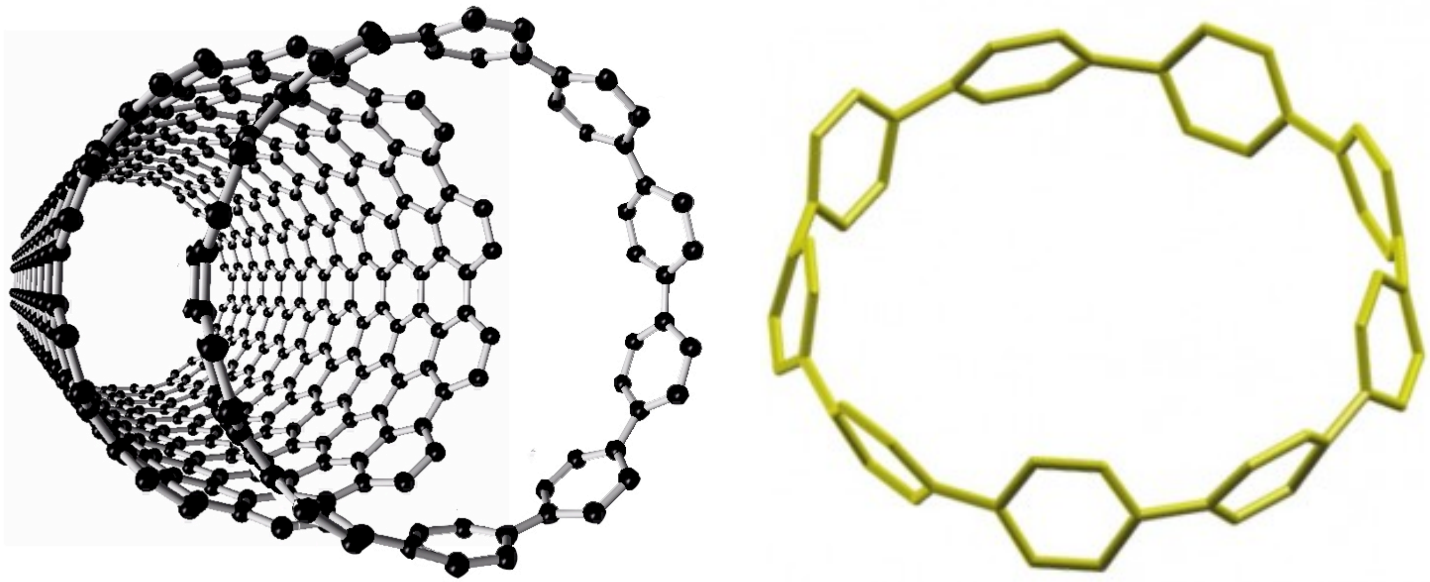
The debut of cycloparaphenylene is well-timed, coming as scientists are working to improve and systematize the way carbon nanotubes are produced. The challenge, however, lies in using it to grow much longer identical carbon nanotubes in a controlled manner.

C. Bertozzi, Director, Molecular Foundry (510)643-1682, Materials Sciences Division (510 486-4755), Berkeley Lab.

Ramesh Jasti, Joydeep Bhattacharjee, Jeffrey B. Neaton, and Carolyn R. Bertozzi, "Synthesis, Characterization, and Theory of [9]-, [12]-, and [18]Cycloparaphenylene: Carbon Nanohoop Structures," *J. Am. Chem. Soc.* 130, 17646-17647 (2008).

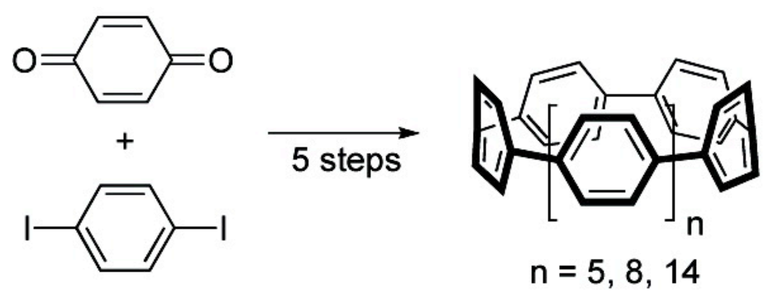
Carbon Nanohoops

Shortest Segment of a Carbon Nanotube Synthesized



An example of the shortest possible carbon nanotube: a "nanohoop" of benzene rings. Figure shows such molecules, called cycloparaphenylenes; one with 9 such rings (above right), and one with 11 rings (above left).

Synthesis of cycloparaphenylene requires the bending of a string of benzene rings—which normally resist bending—into a hoop. The calculated strain energy is considerable, and increases with decreasing ring size: 5, 28, and 47 kcal/mol for hoops with 18, 12, and 9 benzene units, respectively. By carefully selecting small molecule precursors (right), strain was built up sequentially during the synthesis, and rings with 18, 12 and 9 benzenes were obtained in good yield (>35%).



diameters of 1.2, 1.7,and 2.4 nm, respectively